



Simultaneous electrocatalytic reduction of dinitrogen and carbon dioxide on conducting polymer electrodes

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ABSTRACT

The conversion of carbon dioxide with nitrogen containing compounds into valuable materials consisting of C–N bond is a very attractive research area due to today's energy requirements. The simultaneous electrocatalytic reduction of carbon dioxide and dinitrogen was investigated at 60 bar (30 bar N_2 + 30 bar CO_2) in this study. The electrochemical reduction was achieved on polyaniline (PAni) and polypyrrole (PPy) coated platinum electrodes at -0.165 V, the lowest possible overpotentials, known in the literature. The main products from the CO_2 and N_2 reduction were ammonia, urea and formic acid. The electrochemical reduction performed in an aqueous 0.1 M Li_2SO_4 /0.03 M H^+ solution was characterized by using cyclic voltammetry, potentiostatic electrolysis and Tafel diagrams in order to analyze the polymer selectivity as well as its reactivity as a function of the applied potential. Hence, CO_2 and N_2 were converted into value added chemicals, which included urea; an important raw material for the chemical industry with high nitrogen content.

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1. Introduction

The reduction of dinitrogen to ammonia is a natural process, which is conducted by certain micro-organisms using a nitrogenase enzyme. When this essential chemical process occurs in nature it is based -like almost all natural processes- on a sensitive dynamic equilibrium. However, this process is too slow for use at a technical scale and a large amount of energy is needed for the reduction due to the strong triple bond in the N_2 molecule [1–4].

Many attempts have failed to reduce N_2 to amine on bulk metal catalysts due to the fast hydrogen evolution and chemical inactivity of N_2 [5,6]. In addition, based on the operating principles of chlorophyll, some organometallic compounds have been employed to reduce N_2 [7–10].

Due to the similarity to photosynthesis, researchers were stimulated to convert CO_2 under laboratory conditions into organic compounds. Different methods were proposed for CO_2 reduction with homogeneous and heterogeneous systems [11–17]. Among these methods, electrochemical reduction appears to be the most appropriate one, which is why the electro-reduction of CO_2 to valuable products became the aim of many studies with substantial

interest in the recent time [18]. This interest was inspired, firstly, by the need to prevent the greenhouse effect, in which CO_2 plays a primarily role, and secondly, by it being an economic C-source available in huge amounts in the atmosphere.

Employing bulk metal catalysts for CO_2 reduction leads to different substances depending on the metal used as the electrode and on the electrolyte [19]. In an aqueous acidic medium, the main substances are $HCOOH$ and CO . Nevertheless, the application of an aprotic medium leads mostly to hydrocarbons. Although the handling of bulk materials is easy, bulk metal electrodes have the disadvantages of a reduction that occurs at relatively high negative overpotentials. In the literature, the best results were obtained between -1.8 to -1.9 V. However, these high overpotential values could be decreased to ca. -0.4 V by the application of conducting polymers, deposited on the metal surface, in aprotic as well as in aqueous media [14,20].

Urea is commercially produced by the reaction of ammonia and carbon dioxide at a high pressure (100–200 atm) and temperature (about 180 °C). The reaction product, ammonium carbamate, dehydrates rapidly to urea and water. Due to the high energy requirement of these thermic processes, new methods are needed that can convert carbon dioxide, dinitrogen and hydrogen to nitrogen containing substances under mild conditions [21]. It should be emphasized that in contrast to the H^+ and CO_2 reduction, only a few electrocatalysts have been reported to exhibit any activity for N_2 reduction. There are also very few studies on the simultaneous

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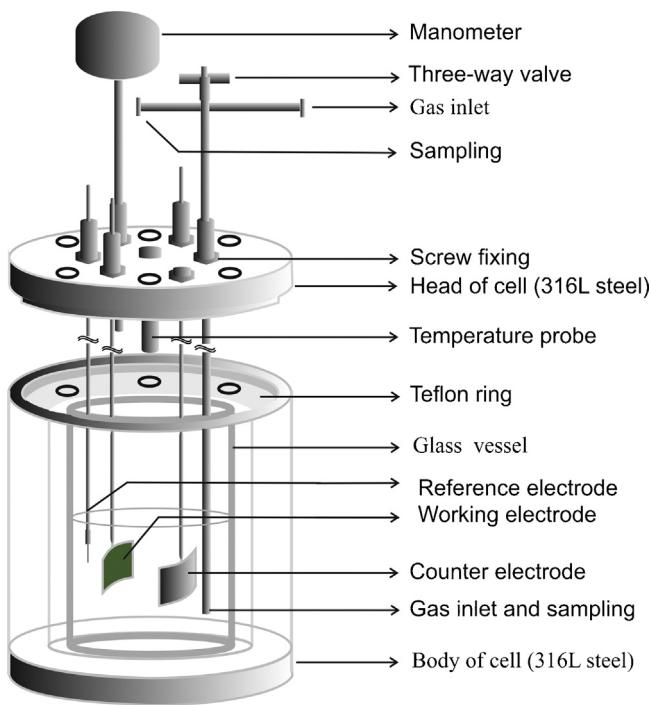


Fig. 1. High pressure cell.

reduction of carbon dioxide and nitrogen containing materials in the literature [22–26].

The electrochemical reductions of N₂ and CO₂ were investigated separately in aqueous medium in our previous studies [27–29], and we could reduce these substances with the application of the lowest possible overpotential values (−0.4 V NHE) – from the literature – to valuable substances. Now, we present the results of a simultaneous, one step reduction of both N₂ and CO₂ gases, in the same ambiance to the obtain urea with the lowest possible energy input (overpotential) on polyaniline and polypyrrole coated platinum electro-catalysts, for the first time.

2. Experimental

Polyaniline and Polypyrrole films were deposited on a Pt plate (8 cm²) by cyclic voltammetry technique. Polymerization of aniline was achieved from solution containing 0.1 M aniline in 0.5 M H₂SO₄. At the first polarization cycle the potential swept between −0.20 V and +1.20 V [Ag/AgCl], the other following cycles swept continuously between −0.20 and +0.85 V to protect the film from overoxidation. Scan rate was 0.05 V/s throughout the measurements. Electro-polymerization was performed in a three electrode H-type cell using a platinum plate (8 cm²) as a counter electrode. After polymerization, the coated electrodes were dipped into methanol for a few minutes to take away surplus ions, washed carefully with water and then transferred into the electrochemical high-pressure cell (Fig. 1). Film thicknesses were determined using the charge value of the first anodic peak of the last growth cycle during PAni film formation. The optimum film thickness of the PAni was calculated as 1.52 μm after 35 cycles.

The polypyrrole films were also grown potentiodynamically from solution containing 0.1 M pyrrole/0.5 M LiClO₄/acetonitrile by cycling the potential from 0.00 V to +1.45 V for the first cycle and 0.00 V to +0.90 V for the following cycles at a scan rate of 0.05 V/s. The thicknesses of the PPy layer were calculated by coulometric oxidation technique as 0.73 μm after 5 cycles.

The coated samples were rinsed thoroughly first with methanol and then water for removing the residual reactants from the polymer films.

The simultaneous reduction of dinitrogen and carbon dioxide was achieved in an electrochemical high-pressure cell where the coated polymer electrodes were used as working electrodes. The counter electrode was a Pt plate (8 cm²) and a Pb(Hg)_x/PbSO₄/SO₄²⁻ was used as a reference electrode with reference potential −0.1 V[NHE]. An Electrochemical Workstation (CHI 660B) was employed for voltammetric measurements between −0.1 V and −0.325 V [NHE]. The preparative electrolysis time was determined experimentally as 5 h. The amounts of ammonia and/or urea produced in the electrolyte were established by the spectrophotometric indophenol method [30].

The reduction product of CO₂ was only formic acid (formate) and it was analysed by HPLC [Agilent 1200; ODS-H-OL column; UV/Vis detector (210 nm); carrier phase: H₂SO₄ solution pH 4; flow rate 2 ml/min]. After electrolyses, a gas sample (1.0 ml) was taken and analyzed by GC (HP 6810; Porapak-QS; FID; 50 °C; He as carrier gas) for possible production of gaseous products.

All reactions were carried out in aqueous 0.1 M Li₂SO₄/0.03 M H⁺, under total pressure of 60 bar including 30 bar N₂ and 30 bar CO₂.

3. Results and discussion

The simultaneous electrochemical reduction of dinitrogen and carbon dioxide was investigated on polymer coated Pt-plate electrodes using both cyclic voltammetry and constant potential electrolysis techniques. Polyaniline and polypyrrole were used to modify the bulk metal surface. These two polymeric materials showed different behaviours in current density and product yields. Control experiments were done on the blank Pt electrode at all applied potential range under 30 bar N₂ and 30 bar CO₂ atmosphere in order to ensure the activity of the deposited conducting polymers and also under 60 bar Ar on the PAni and PPy coated Pt electrode under same conditions. There was no product formation in both cases.

3.1. Voltammetric investigations

The cyclic voltammograms (CV) of the PAni-coated and PPy-coated Pt electrodes are presented in Fig. 2.

Fig. 2 shows the CVs of the PAni and PPy coated Pt plate electrodes (8 cm²) under a total pressure of 60 bar (30 bar N₂ + 30 bar CO₂) in 0.1 M Li₂SO₄/0.03 M H⁺. These CVs show the main features of the electro-reduction of the proton to form an atomic hydrogen (H_{ad}). In other words, the electrode process comprises an electron transfer step followed by the possibly of a slow chemical step via Reactions 1–3 as shown below.



During the measurements/preparative electrolyses, the reduction current was noticeably higher at the PPy coated electrode than the PAni; this result was also verified by the product formation. Therefore, we could determine the higher product concentrations on the PPy modified catalysts.

3.2. Electro-reduction on PAni coated Pt electrode

The reaction products of the simultaneous electrochemical reduction of dinitrogen and carbon dioxide were ammonia, urea

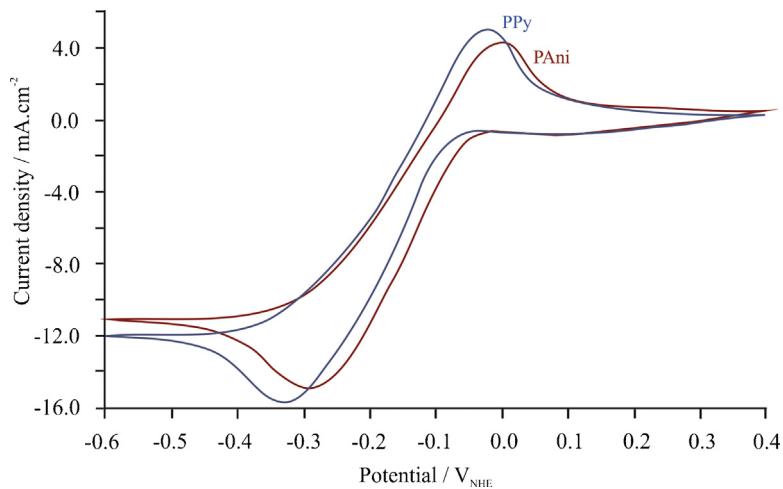


Fig. 2. The cyclic voltammograms of the PAni and PPy coated electrodes in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ at 30 bar N₂ + 30 bar CO₂, $v = 0.05$ V/s.

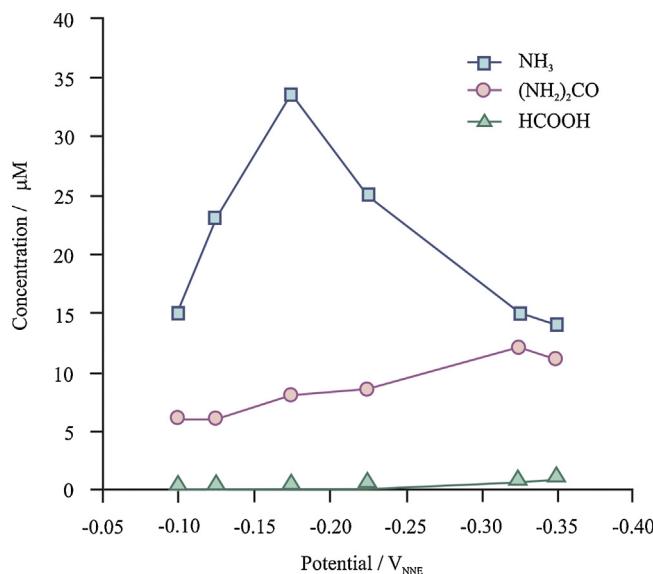


Fig. 3. The concentration of reduction products on the PAni electrode after 5 h of electrolysis in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution at room temperature, as the function of applied potential (30 bar CO₂ + 30 bar N₂).

and formic acid. Fig. 3 shows the relation between electrode potential and concentration of products of the simultaneous reduction at polyaniline deposited on the Pt electrode in the presence of N₂ and CO₂ in the high pressure cell with partial pressures of 30 bars for each gas. The reduction was performed under different potentials that varied from -0.1 V to -0.35 V (NHE). We know that the main product of the electrochemical reduction of CO₂ in aqueous medium is formic acid [27,31–34]. In the case of a polymer coated electrode, the formic acid formation starts at -0.1 V, but the reaction rate is too low due to the extremely low current values. It becomes more interesting up to -0.125 V, which is why we performed the measurements by stepwise increasing the potential to record every change in the concentration depending on the applied potential.

The concentrations of the reduction products on the PAni electrode after 5 h of electrolysis in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution at room temperature are presented in Fig. 3.

The concentration of ammonia reached a maximum after 5 h near -0.165 V, and then it decreased dramatically at potentials

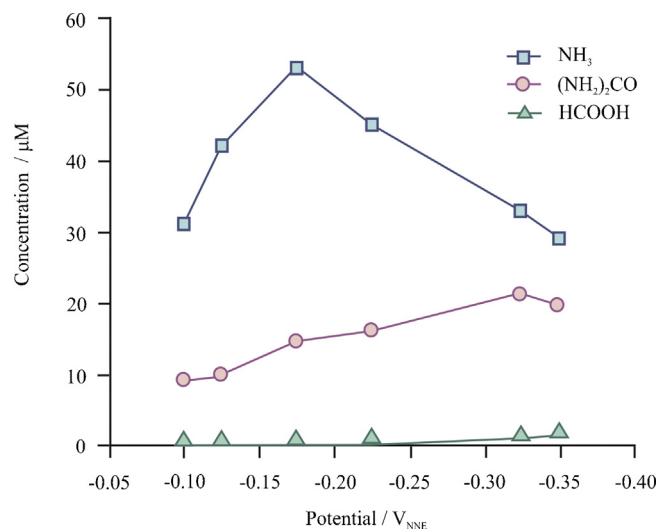


Fig. 4. The concentration of reduction products on the PPy electrode after 5 h of electrolysis in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution at room temperature, as a function of potential (30 bar CO₂ + 30 bar N₂).

more cathodic than -0.165 V, which was accompanied by significant hydrogen evolution.

As noticed previously, these processes have sensitive equilibria, and out of the range of the optimum potential and pressure values, product yields dropped remarkably. The optimum potential values obtained experimentally are presented in Fig. 3. The experiments began at -0.1 V and ended at -0.35 V. After -0.3 V the formation of ammonia decreased, and the reduction of CO₂ became remarkable. According to these results, we stopped the reactions at -0.35 V, and unfortunately, the metal-polymer combination of the electrode does not allow any operation at more negative values than -0.4 V due to the crumbling of the coating material from the metal surface due to the strong hydrogen evolution. Note that, H₂ evolution is always in competition with CO₂ reduction in aqueous systems [35].

3.3. Electro-reduction on PPy coated Pt electrode

The Pt electrode coated with the polypyrrole film lead to much more valuable results under the same conditions as with the PAni electrode (Fig. 4).

Table 1

Concentrations of formed products of reduction versus applied potential on PAni and PPy coated Pt electrocatalyst in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution after 5 h electrolysis time.

| Potential/V _{NHE} | Product concentrations/ μM | | | | | |
|----------------------------|---------------------------------------|----------------------|-------|-----------------|----------------------|-------|
| | PAni | | | PPy | | |
| | NH ₃ | (NH ₂)CO | HCOOH | NH ₃ | (NH ₂)CO | HCOOH |
| -0.100 | 15.0 | 6.0 | – | 31 | 9.4 | – |
| -0.125 | 23.0 | 6.0 | – | 42 | 10.0 | – |
| -0.165 | 33.5 | 8.0 | 0.02 | 53 | 14.5 | 0.045 |
| -0.225 | 25.0 | 8.5 | 0.03 | 45 | 16.1 | 0.052 |
| -0.325 | 15.0 | 12.0 | 0.56 | 33 | 21.2 | 0.680 |
| -0.350 | 14.0 | 11.0 | 0.72 | 29 | 19.7 | 0.910 |

Table 2

Current efficiencies resulting from the electrolyses on PAni and PPy coated Pt electrocatalyst in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution after 5 h electrolysis time.

| Potential/V _{NHE} | Faradaic efficiencies/% | | | | | |
|----------------------------|-------------------------|----------------------|-------|-----------------|----------------------|-------|
| | PAni | | | PPy | | |
| | NH ₃ | (NH ₂)CO | HCOOH | NH ₃ | (NH ₂)CO | HCOOH |
| -0.100 | 4.5 | 2.0 | – | 7.4 | 5.2 | – |
| -0.125 | 9.8 | 2.2 | – | 15.9 | 5.4 | – |
| -0.165 | 10.5 | 3.1 | 2.7 | 18.1 | 6.5 | 3.8 |
| -0.225 | 9.1 | 3.5 | 2.9 | 17.4 | 7.1 | 4.8 |
| -0.325 | 8.0 | 3.4 | 3.3 | 16.2 | 6.9 | 5.2 |
| -0.350 | 7.0 | 4.8 | 4.1 | 15.8 | 5.7 | 6.1 |

The concentration of ammonia reached a peak value of 53 μmol at around -0.165 V and then decreased again with increasing potential in negative direction.

The highest concentration of ammonia was found at -0.165 V . In the negative direction, the concentration of ammonia decreased and the concentration of urea increased up to -0.325 V . The highest urea concentration was found to be 21.2 μmol at -0.325 V . At more negative potentials, ammonia and urea formation began to decrease because the conductivity of the electrode dropped.

The results of the experiments carried out under 60 bar are summarized in **Table 1** including product concentrations and **Table 2** including current efficiencies.

The results are largely dependent on the applied potential and the coating material.

Although we did not study the effect of the electrolyte medium and polymer film thickness in this work, we have obtained the best results in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution and 1.52 μm thickness for PAni and 0.73 μm thickness for PPy as mentioned in our previous study; it was determined that the electrolyte medium and film thickness could change the product efficiency remarkably [28]. We reported in our previous studies, coating of a metal surface with conducting polymers causes a controlled formation of H-atoms, which have a great ability to reduce carbon dioxide, nitrogen as well as nitrate ions at extremely low potentials [36,37]. The thickness of the film is also a very important parameter for this process; in the case of very thick film, the current decreases due to the coating of the metal surface completely; in the case of a too thin film, the metallic character becomes dominant. The chance of the combination of H_{ad} with the reducing molecule (N₂ or CO₂) decreases in both cases.

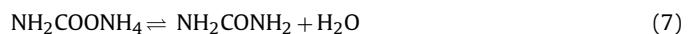
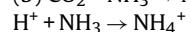
The SEM images of PAni and PPy coated Pt electrode are shown in the **Fig. 5**. The films are in porous structure that have a large surface area and this helps to enhance the catalytic activity of the electrode.

3.4. Mechanism

Ammonia and carbon dioxide reacted under pressure to form ammonium carbamate: in this case ammonia was synthesized from N₂ in the solution which became carbamate via a chemical step with CO₂ [38]. In the first step a proton was reduced to an atomic hydrogen (Reaction (1)); the H_{ad}'s were added to N₂ and the reaction product ammonia was formed (Reaction (4)).



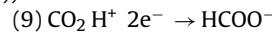
Under the reaction conditions, ammonia reacted with CO₂ to form the species NH₂COO[−] (Reaction (5)), and the further steps led to carbamate.



Therefore, the overall reaction could be formulated as follows:



As mentioned previously, at more negative potentials, CO₂ reduction begins and the reaction product is formic acid (Reaction (9)).



The reaction pathway formulated above appears to be very plausible because the protons in the electrolyte solution act as a reaction component and the formed atomic hydrogen reduces the other species available in the electrolyte, such as N₂ and CO₂, to the end-products. Otherwise, an electron transfer onto N₂ and/or CO₂ needs much more energy than was used in this process [34]. These suggestions are supported with Tafel diagrams recorded for both polymer electrodes, which are presented in **Fig. 6**.

Tafel analyses were performed using the Tafel equation based on the Butler–Volmer equation:

$$j = \frac{j_0 \exp \alpha \eta F}{RT} = \frac{j_0 \exp \eta}{b_c} \quad (10)$$

where j, current density; j₀, exchange current density; α, transfer coefficient; η, over potential; F, Faraday's constant; R, universal gas constant; T, absolute temperature; and b_c, cathodic Tafel slope. The Tafel slope can be calculated by arranging Eq. (10) in logarithmic form.

$$\frac{\delta \eta}{\delta \log j} = \frac{-2.3RT}{\alpha nF} \quad (11)$$

The Tafel slopes for both polymeric materials (PAni and PPy), calculated from Eq. (11), gave values of 127 and 121 mV/dec, respectively. Both values are close to 120 mV/dec; the value corresponding to one electron reaction of the charge transfer. These calculated values clearly support that the reaction is via atomic hydrogen [27,28,37,39].

Additionally, the activation energy could be calculated using the Arrhenius law for both electrodes:

$$\log j_0 = \frac{-E_a}{RT + \ln A_0} \quad (12)$$

Arrhenius plots of the logarithm current density (lnj) at -0.165 V versus the reciprocal of the absolute temperature (T^{-1}) that provided the activation energies from their slopes for both electrodes are shown in **Fig. 7**.

The calculated activation energies for PAni and PPy of 29.8 kJ/mol and 32.6 kJ/mol, respectively, are in the range of hydrogenation reactions in protic media. The Tafel slopes and activation

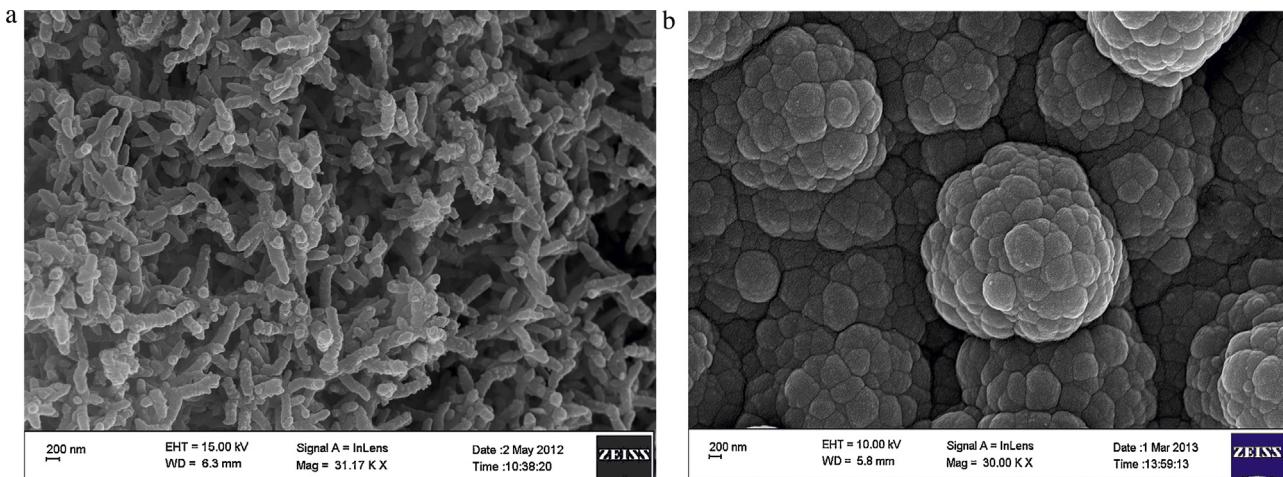


Fig. 5. The SEM images of PAni (a) and PPy (b) coated Pt electrode.

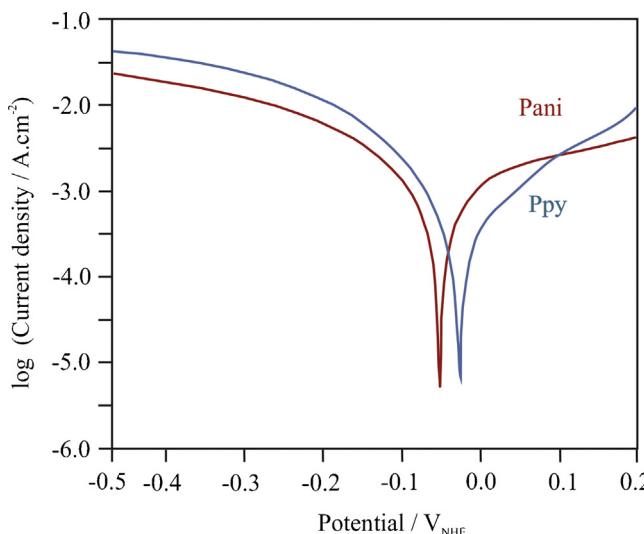


Fig. 6. The Tafel curves of the PAni and PPy coated electrodes in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ at 30 bar N₂ + 30 bar CO₂, v = 0.001 V/s.

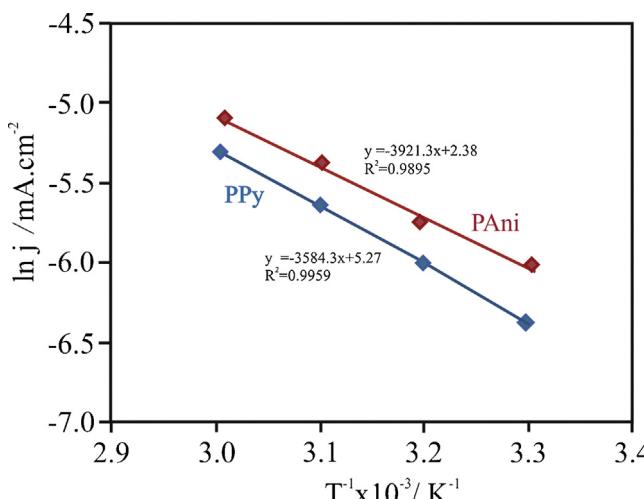


Fig. 7. The logarithm of current density as a function of 1/T at -0.165V[NHE] on PAni and PPy coated Pt electrodes in aqueous 0.1 M Li₂SO₄/0.03 M H⁺ at 30 bar N₂ + 30 bar CO₂.

energy values are typical for Volmer type reactions [39], and as suggested, the reduction of nitrogen is a simple hydrogenation, as shown in Reactions (1)–(3). The formation of carbamate is a chemical step. As stated previously, we could only detect ammonia and urea in the electrolyte. Any other possible products, such as hydrazin and/or formamide, could not be found after careful analysis for these substances by hydroxamate methods [40].

4. Conclusion

A novel synthesis method for urea was identified in the present study. Dinitrogen and CO₂ were simultaneously reduced on two different conducting polymer electrodes, namely on polyaniline and polypyrrole, in an aqueous 0.1 M Li₂SO₄/0.03 M H⁺ solution at room temperature as a function of potential and polymer film under 60 bars (30 bar CO₂ + 30 bar N₂). We found that polypyrrole catalysed the N₂ reduction more effectively than polyaniline. We determined that the optimum potential was -0.165 V, and the maximum yield of ammonia at that potential was 33.5 and 53 μmol for the polyaniline and polypyrrole, respectively. In addition, for urea formation, polypyrrole appears to be the better material. Depending on the ammonia concentration in the solution, the urea concentration increased up to -0.325 V to a maximum value of 21.2 μmol on polypyrrole and 12 μmol on polyaniline.

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